

PATENT ABSTRACTS OF JAPAN

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(54) AQUEOUS INK COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an aqueous ink composition which is excellent in both setting stability and storage stability by dispersing, in an aqueous medium, a surface-modified pigment dispersible and/or dissolvable in water in the absence of a dispersant and by adjusting the concentration of a free polyvalent anion in the ink to a specified value or lower.

SOLUTION: The concentration of the free polyvalent anion in the ink is adjusted to 250 ppm or lower. Sulfate, phosphate, and low-mol.-wt. polycarboxylate ions, etc., are listed as the polyvalent anion. Preferable pigments to be surface-modified are carbon black and organic pigments. Especially preferably, the surface-modified pigment is prepared by oxidizing carbon black or an organic pigment with a halogenic acid compound (e.g. sodium hypochlorite or hypobromite). The cocentration of the free monovalent anion in the ink can be decreased preferably by purifying a dispersion containing the surface-modified pigment oxidized and dispersed therein by reverse osmosis, ultrafiltration, electrodialysis, or the like and then preparing the ink.

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CLAIMS

[Claim(s)]

[Claim 1] The water-color-ink constituent characterized by the multiple-valued anion concentration from which it is the water-color-ink constituent which contains without an aqueous medium and a dispersant in water at least the surface treatment pigment in which distribution and/or the dissolution are possible, and was isolated in said ink being 250 ppm or less.

[Claim 2] The water-color-ink constituent according to claim 1 characterized by said multiple-valued anion being sulfate ion.

[Claim 3] A water-color-ink constituent given in any 1 term of claims 1-2 to which said surface treatment pigment is characterized without the dispersant oxidized and obtained with the halogen acid compound in carbon black by being the surface treatment pigment in which distribution and/or the dissolution are possible at water.

[Claim 4] A water-color-ink constituent given in any 1 term of claims 1-2 to which said surface treatment pigment is characterized without the dispersant oxidized and obtained with the halogen acid compound in the organic pigment by being the surface treatment pigment in which distribution and/or the dissolution are possible at water.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the distributed process input output equipment water color ink which used carbon black or an organic pigment as a coloring agent. It is related with amelioration of the water-color-ink constituent which contains in water the surface treatment pigment in which distribution and/or the dissolution are possible in more detail.

[0002]

[Description of the Prior Art] As for the recording ink used for the writing implement and ink jet printer of the conventional aqueous, the water-soluble color has been used. In order to improve the image quality and endurance of a record object in recent years, pigments, such as carbon black, are used for a coloring agent.

[0003] For example, the watercolor pigment ink which distributed carbon black with the surfactant or the macromolecule dispersant is indicated by JP,64-6074,A and JP,64-31881,A.

[0004] However, if the ink content of a coloring agent is increased in order to raise the printing concentration of a record object in these ink, the problem which ink viscosity increases rapidly to coincidence will arise. Moreover, in order to distribute to stability, a superfluous surfactant and a macromolecule dispersant are required, but these cause gassing and an antifoam fall, and when it uses especially for ink jet record ink, they have the problem which leads to aggravation of printing stability.

[0005] In order to solve these technical problems, the surface activity hydrogen more than a constant rate or its salt is introduced into carbon black, and the dispersion liquid using the surface treatment carbon black which can be spontaneously distributed by the carbon black independent processed without the surface active agent or the giant-molecule dispersant are indicated by JP,8-3498,A and JP,10-120958,A. Furthermore, the ink jet ink containing above-mentioned surface treatment carbon black and glycol ether is proposed by JP,10-95941,A. Moreover, adjusting the total sulfur and all the chlorinity of carbon black to less than [0.1wt%] in order to promote ionization of the functional group in surface treatment carbon black is indicated by JP,10-212426,A.

[0006]

[Problem(s) to be Solved by the Invention] It is very effective, concerning hypoviscosity-izing and printing stability of ink with the ink using the surface treatment carbon black which can be distributed spontaneously as mentioned above. However, the ionicity matter which originates in the sulfur desorbed from the pigment itself according to the surface treatment process for making it distribute spontaneously is generated. In the watercolor pigment ink which distributed the carbon black indicated by JP,64-6074,A and JP,64-31881,A with the surfactant or the macromolecule dispersant, although there was no cause which the above-mentioned ionicity matter generates at a distributed process, when comparatively a lot of ionicity matter was generated and there was these ionicity matter in large quantities, with the surface treatment pigment, it was found out that thickening etc. arises when ink is saved for a long period of time, and preservation stability falls.

[0007] Therefore, this invention aims at offering a water-color-ink constituent with still higher

preservation stability in the water-color-ink constituent which contains without a dispersant in water the surface treatment pigment in which distribution and/or the dissolution are possible, improving printing stability.

[0008]

[Means for Solving the Problem] The water-color-ink constituent of this invention is characterized by the multiple-valued anion concentration from which it is the water-color-ink constituent which contains without an aqueous medium and a dispersant in water at least the surface treatment pigment in which distribution and/or the dissolution are possible, and was isolated in said ink being 250 ppm or less.

[0009]

[Embodiment of the Invention] The water-color-ink constituent of invention distributes in water the surface treatment pigment in which distribution and/or the dissolution are possible without dispersants, such as a surfactant and water soluble resin, in an aqueous medium. Furthermore, the multiple-valued anion concentration which separated in ink adjusts to 250 ppm or less.

[0010] In this invention, even if a pigment does not use a dispersant, the condition of existing in stability with the minimum particle diameter which can be distributed underwater is expressed as "distribution and/or the dissolution." The minimum particle diameter which can be distributed is the minimum particle diameter which does not become small any more even if it increases distributed time amount. It is thought with the minimum particle diameter which can distribute a pigment that it distributes spontaneously so that water soluble dye may dissolve in water by the single molecule, because introduce a hydrophilic functional group in large quantities and it carries out surface treatment to the front face of carbon black or an organic pigment.

[0011] Surface treatment for "distributing and/or dissolving" is performed by combining hydrophilic functional groups, such as a carboxyl group, a carbonyl group, and hydroxyl, and the salt of those through direct or alkyl, alkyl ether, an aryl group, etc. on the surface of a pigment. The approach to which a pigment front face is made to specifically carry out the graft of the active species containing the approaches of oxidizing with an oxidizing agent and introducing [hydroxyl / a carboxyl group, / a carbonyl group, hydroxyl] a pigment front face underwater, these functional groups, or a functional group by chemical preparation is raised.

[0012] As for the water color ink of this invention, it is desirable to add a surface treatment pigment in 1 - 15% of range to the ink whole quantity. If it is this range, the water color ink of sufficient printing concentration can be obtained.

[0013] In the addition of an above-mentioned surface treatment pigment, if the isolation multiple-valued anion concentration in the ink of the water color ink of this invention is 250 ppm or less, even if it leaves ink for a long period of time, it does not have thickening etc., and can obtain ink with sufficient preservation stability. As a multiple-valued anion, sulfate ion, phosphoric-acid ion, and low-molecular polycarboxylic acid are mentioned. Since the sulfur contained in the pigment itself from the first ***** at a distributed process, it oxidizes by the halogen acid salt further used for the wet oxidation for surface treatment and serves as a sulfuric acid, it is easy to mix especially sulfate ion in large quantities. For this reason, removing to 250 ppm or less is desirable.

[0014] Reduction of the isolation multiple-valued anion concentration in ink has the desirable approach of creating ink, after refining the dispersion liquid of the surface treatment pigment oxidized and distributed by the reverse osmotic membrane, ultrafiltration, electrodialysis, etc. in order not to worsen the dispersibility of dispersion liquid. Moreover, it is also possible to refine, after adding alkali, such as a sodium hydroxide, and creating a salt.

[0015] The quantum of isolation multiple-valued anion concentration can be performed by the following analytical method. An ultrafiltration filter separates ink into solid content and a liquid component, and a liquid component is diluted with ultrapure water to suitable concentration, and it measures by the ion chromatograph and is obtained.

[0016] In addition, if it does not ***** even if it exists in the interior of a pigment, or adsorbs on a pigment front face strongly and leaves it, even if the whole quantity contained in the ink of the above-mentioned matter exceeds 250 ppm, the long-term preservation stability of ink will not be influenced.

[0017] As for this invention, it is desirable to use carbon black and an organic pigment as a pigment for carrying out surface treatment.

[0018] As an example of desirable carbon black, #20B, #40, MA100, etc. are mentioned as carbon black by Mitsubishi Chemical, Inc. by this invention. As Degussa AG carbon black, the color black FW18, the color black S170, the special black 250, etc. are mentioned. The KONDAKU tex SC, Rahaeng 1255, etc. are mentioned as carbon black by the Colombia carbon company. As carbon black by Cabot Corp., MONAKU 700, MONAKU 880, the elf tex 12, etc. are mentioned. In addition, these are the publications of an example of the suitable carbon black for this invention, and this invention is not limited by these.

[0019] As a desirable organic pigment, an azo system pigment, a phthalocyanine system pigment, an anthraquinone system pigment, the Quinacridone system pigment, a thioindigo system pigment, a triphenylmethane color system lake pigment, an oxazine system lake pigment, etc. are mentioned by this invention. Furthermore, if insoluble to an aqueous medium, the oil color, a disperse dye, etc. can also be used. Specifically as a yellow system, the C.I. pigment yellow 1, 2, 3, 4, 5, 6, 7, 10, 11, 12, 13, 14, 15, 16, 17, 65, and 83 is mentioned. moreover, as a red system C. I. pigment red 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 21, 22, 23, 30, 31, 32, 37, 38, 39, 40, 49, 50, 51, 52, 53, 55, 60, 64, 83, and 87, 88, 89, and 90, 112, 114, 123, 163 grades are mentioned. As a blue system, the C.I. pigment black 1 is mentioned as the C.I. pigment blues 2, 3, 15, 16, and 22, 25 grades, and a black system.

[0020] Moreover, creation of the surface treatment pigment used for the water color ink of this invention has especially the desirable thing that the approach to which a pigment front face is made to carry out the graft of the active species which contained the approaches of oxidizing with an oxidizing agent and introducing [hydroxyl / a carboxyl group / a carbonyl group hydroxyl] a pigment front face underwater, these functional groups, or a functional group by chemical preparation raises, and **** oxidizes and acquires for carbon black or an organic pigment with a halogen acid compound as mentioned above. As a halogen acid compound, a sodium-hypochlorite water solution, a calcium hypochlorite, a hypobromous acid sodium water solution, a hypoiodous acid sodium water solution, etc. are mentioned. In addition, since the following ** fluorine acid is very unstable, it cannot be substantially used for creation of a surface treatment pigment.

[0021] The aqueous medium of the water-color-ink constituent of invention is a medium for holding a surface treatment pigment, and can give the property as ink, and can add a fixing agent, pH regulator, an antioxidant and an ultraviolet ray absorbent, antiseptics, an antifungal agent, etc. further if needed including water, a moisturizer, and an osmosis accelerator at least.

[0022] Desirable water can use pure water, such as ion exchange water, ultrafiltration water, Milli Q water, and distilled water, or ultrapure water for this invention. Moreover, since generating of mold or bacteria can be prevented when carrying out the mothball of the ink constituent if the water which sterilized by UV irradiation or hydrogen-peroxide addition is used, it is suitable.

[0023] As a moisturizer which can be used for this invention It is chosen out of a water-soluble and hygroscopic high ingredient. A glycerol, ethylene glycol, A diethylene glycol, triethylene glycol, tetraethylene glycol, A polyethylene glycol, propylene glycol, dipropylene glycol, A polypropylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol 1,6-hexanediol, 1 and 2, 6-hexane triol, Polyols, such as pentaerythritol, 2-pyrrolidone, a N-methyl-2-pyrrolidone, Saccharides, such as ureas, such as RAKURAMU [, such as epsilon caprolactam,], urea, thiourea, ethylene urea, 1, and 3-dimethyl imidazolidinone, maltitol, a sorbitol, glucono lactone, and a maltose, can be used.

[0024] These moisturizers can be added with the addition from which ink viscosity is set to 25 or less cPses at 25 degrees C together with other ink additives.

[0025] As an osmosis accelerator which can be used for this invention, permeability is brought forward by improving the wettability to a record medium, and it is chosen out of the water-soluble organic solvent and surfactant with which the surface tension of a water solution becomes small.

[0026] As a water-soluble organic solvent, 1, such as carbitol [, such as cellosolves, such as lower alcohol, such as ethanol and propanol, ethylene glycol monomethyl ether, and ethylene

glycol monoethyl ether the diethylene-glycol monomethyl ether, diethylene glycol monoethyl ether, ethylene glycol mono-n-butyl ether, diethylene-glycol-n-butyl ether, and triethylene glycol-n-butyl ether,], 1, 2-hexandiol, 1, and 2-octanediol, and 2-alkyl diols are raised.

[0027] Moreover, as a surfactant, acetylene glycol system Nonion nature surfactants, such as the Nonion nature surfactants, such as anionic surfactants, such as fatty-acid salts and alkyl-sulfuric-acid ester salts, polyoxyethylene alkyl ether, and polyoxyethylene phenyl ether, and SAFI Norians 61 and 82,104,440,465,485 (all are trade name and air products - and made in - Chemicals above), a cationic surfactant, both ionic surfactants, etc. can be used.

[0028] In addition, without using for the surface treatment pigment of this invention the dispersant which consists of a surfactant, since it is the coloring agent in which distribution and/or the dissolution are possible, these surfactants used in the ink of this invention can be used for water only for promotion of osmosis. That is, although it is necessary to choose in the combination to which a pigment and each ingredient stick each other in order to usually give dispersibility to a pigment, by this invention, it can choose only by osmosis promotion nature, without taking combination into consideration.

[0029] Water-soluble resin can be used as a fixing agent. Water-soluble rosin Alginic acids, polyvinyl alcohol, hydroxypropylcellulose, A carboxymethyl cellulose, hydroxyethyl cellulose, methyl cellulose, Styrene-acrylic acid resin, styrene-acrylic-acid-acrylic ester resin, Styrene-maleic resin, styrene-maleic-acid half ester resin, Acrylic-acid-acrylic ester resin, isobutylene-maleic resin, rosin denaturation maleic resin, a polyvinyl pyrrolidone, gum arabic starch, the poly allylamine, a polyvinyl amine, polyethyleneimine, etc. are mentioned. In addition, without using for the surface treatment carbon black of this invention the dispersant which consists of water soluble resin, since it is the coloring agent in which distribution and/or the dissolution are possible, the water soluble resin used in the ink of this invention can be used for water only for fixing. That is, although it is necessary to choose in the combination to which a pigment and each ingredient stick each other in order to usually give dispersibility to a pigment, by this invention, it can choose only by fixable, without taking combination into consideration.

[0030] As a pH regulator, the hydroxide or amines of alkali metal, such as a lithium hydroxide, a sodium hydroxide, a potassium hydroxide, aqueous ammonia, triethanolamine, and diethanolamine, are mentioned.

[0031] as an anti-oxidant and an ultraviolet ray absorbent — aloha — NETO and methyl aloha — NETO etc. — aloha, the oxide of lanthanides, such as Ciba-Geigy Tinuvin(s) 328, 900, 1130, 384, 292, 123, 144, 622, 770, and 292, such as L-ascorbic acid, such as biurets, such as NETO, biuret, dimethyl biuret, and tetramethyl biuret, and a salt of those, Irgacor 252 and 153, Irganox 1010, 1076, and 1035, and MD1024, etc. is used.

[0032] As antiseptics and an antifungal agent, it can choose, for example from sodium benzoate, pentachlorophenol sodium, 2-pyridine thiol-1-oxide sodium, sodium sorbate, sodium-dehydroacetate, 1, and 2-JIBENJISO thiazoline-3-ON (pro cheating-on-the-fare XL- the pro cheating on the fare CRL of ICI, the pro cheating on the fare BDN, the pro cheating on the fare GXL, 2, pro cheating on the fare TN) etc.

[0033]

[Example] (Example 1) MA8 (trade name, Mitsubishi Chemical, Inc. make) 100g was mixed in 1kg of water as carbon black, and the ball mill by zirconia beads ground. 400g of sodium-hypochlorite water solutions was added to this grinding undiluted solution, it boiled for 10 hours, and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. This wet cake was re-distributed in 5kg of water, and the ultrafiltration membrane of a cut off molecular weight 100,000 was used with the mini tongue (a trade name, Millipore Corp. make) of an ultrafiltration system, and it desalted and refined to electric conductivity 4 mS/cm, condensed to pigment concentration 15wt% further, and pigment dispersion liquid were adjusted.

[0034] The obtained pigment dispersion liquid were mixed as 30g and a moisturizing component, tert-pentanol 4g and Nissan Nonion NS-220(trade name, Nippon Oil & Fats Co., Ltd. make) 1g of the Nonion nature surfactant were mixed as glycerol 10g, 2-pyrrolidone 5g, and an osmosis

promotion component, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.5. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and water color ink was prepared.

[0035] It is a centrifugal type ultrafiltration unit about water color ink. As a result of separating a liquid component using the ultra free-lancer 15/a cut off molecular weight 10,000 (a trade name, Nihon Millipore make) and measuring a liquid component by ion chromatograph DX-500 (Nippon Daionekusu make), the concentration of isolation multicharged ion was 105 ppm in sulfate ion.

[0036] It is a centrifugal type ultrafiltration unit about water color ink. As a result of separating a liquid component using the ultra free-lancer 15/a cut off molecular weight 10,000 (a trade name, Nihon Millipore make) and measuring a liquid component by ion chromatograph DX-500 (Nippon Daionekusu make), the concentration of isolation multicharged ion was 105 ppm in sulfate ion.

[0037] (Example 2) Demineralization / purification degree was performed by electric conductivity 10 mS/cm to the example 1, and water color ink was created similarly. The concentration of the sulfate ion which separated was 250 ppm.

[0038] (Example 3) Color black S170 (trade name, Degussa AG make) 40g was mixed in 1kg of water as carbon black, and the ball mill by zirconia beads ground. 400g of sodium-hypochlorite water solutions was added to this grinding undiluted solution, it boiled for 10 hours, and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. This wet cake was re-distributed in 5kg of water, and the ultrafiltration membrane of a cut off molecular weight 100,000 was used with the mini tongue (a trade name, Millipore Corp. make) of an ultrafiltration system, and it desalted and refined to electric conductivity 4 mS/cm, condensed to pigment concentration 15wt% further, and pigment dispersion liquid were adjusted.

[0039] The obtained pigment dispersion liquid were mixed as 35g and a moisturizer, diethylene-glycol-Monod n-butyl ether 7.5g was mixed as glycerol 10g, diethylene-glycol 5g, and an osmosis accelerator, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.3. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and water color ink was prepared.

[0040] As a result of analyzing water color ink by the same approach as an example 1, the concentration of the multiple-valued anion which separated was 200 ppm only in sulfate ion.

[0041] (Example 4) 50g of the C.I. pigment red 163 was mixed in 1kg of water as an organic pigment, and the ball mill by zirconia beads ground. 150g of sodium-hypochlorite water solutions was added to this grinding undiluted solution, and wet oxidation was performed, stirring for 10 hours. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. This wet cake was re-distributed in 5kg of water, and the ultrafiltration membrane of a cut off molecular weight 100,000 was used with the mini tongue (a trade name, Millipore Corp. make) of an ultrafiltration system, and it desalted and refined to electric conductivity 6 mS/cm, condensed to pigment concentration 15wt% further, and pigment dispersion liquid were adjusted.

[0042] SAFI Norian 465 of diethylene-glycol-Monod n-butyl ether 5g and an acetylene glycol system surfactant was mixed as 30g and a moisturizer, 1g was mixed for the obtained pigment dispersion liquid as glycerol 10g, diethylene-glycol 5g, and an osmosis accelerator, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.2. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and water color ink was prepared.

[0043] As a result of analyzing water color ink by the same approach as an example 1, the concentration of the multiple-valued anion which separated was 250 ppm only in sulfate ion. A part of C.I. pigment red 163 decomposes by oxidation of a hypochlorous acid, and sulfate ion is presumed to be desorption and the ionized thing.

[0044] (Example 1 of a comparison) Demineralization / purification degree was performed by electric conductivity 15 mS/cm to the example 1, and water color ink was created similarly. The

sulfate ion concentration which separated was 300 ppm.

[0045] (Example 2 of a comparison) Demineralization / purification degree was performed by electric conductivity 20 mS/cm to the example 3, and water color ink was created similarly. The sulfate ion concentration which separated was 400 ppm.

[0046] MJ-930C (a trade name, Seiko Epson, Inc. make) of the <evaluation approach> (printing stability) piezoelectric-device type on-demand mold ink jet recording device was filled up with the ink of examples 1-4 and the examples 1 and 2 of a comparison, 3000 sheets of forms of A4 were printed continuously, and the stability at the time of printing was evaluated. the count of the need of the cleaning from the case where there is no turbulence of printing over all number of sheets — averaging — every 500 or more sheets — the case of being required — A — averaging — every [from 100 sheets] 500 sheets — the case where cleaning is required — B — less than 100 sheets estimated by setting to C the case where cleaning is required on the average.

[0047] (Preservation stability) The ink of examples 1-4 and the examples 1 and 2 of a comparison was left for one month at 60 degrees C, and the ink viscosity before and behind neglect was measured. The case where the viscosity change before and behind neglect was 95 - 105% of range was evaluated [% / 120 / B, less than 80%, or / or more] by being referred to as C in A and 80 - 120% of case.

[0048] The result of printing stability and preservation stability is collectively shown in Table 1.

[0049]

[Table 1]

実施例	遊離多価 アニオン濃度	印字安定性	保存安定性
実施例 1	105 ppm	A	A
実施例 2	250 ppm	A	B
実施例 3	200 ppm	A	A
実施例 4	250 ppm	A	B
比較例 1	300 ppm	A	C
比較例 2	400 ppm	B	C

[0050] In the examples 1-4 250 ppm or less, printing stability was A, and preservation stability is A or B and the multiple-valued anion concentration which was shown in Table 1 and from which it was isolated in the ink of the requirements for this invention like has offered the water-color-ink constituent with which printing stability and preservation stability were compatible. On the other hand, in the examples 1 and 2 of a comparison in which isolation multiple-valued anion concentration is over 250 ppm, as compared with the example, preservation stability was bad, and it has been incompatible in printing stability and preservation stability.

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TECHNICAL FIELD

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PRIOR ART

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[0004] However, if the ink content of a coloring agent is increased in order to raise the printing concentration of a record object in these ink, the problem which ink viscosity increases rapidly to coincidence will arise. Moreover, in order to distribute to stability, a superfluous surfactant and a macromolecule dispersant are required, but these cause gassing and an antifoam fall, and when it uses especially for ink jet record ink, they have the problem which leads to aggravation of printing stability.

[0005] In order to solve these technical problems, the surface activity hydrogen more than a constant rate or its salt is introduced into carbon black, and the dispersion liquid using the surface treatment carbon black which can be spontaneously distributed by the carbon black independent processed without the surface active agent or the giant-molecule dispersant are indicated by JP,8-3498,A and JP,10-120958,A. Furthermore, the ink jet ink containing above-mentioned surface treatment carbon black and glycol ether is proposed by JP,10-95941,A. Moreover, adjusting the total sulfur and all the chlorinity of carbon black to less than [0.1wt%] in order to promote ionization of the functional group in surface treatment carbon black is indicated by JP,10-212426,A.

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TECHNICAL PROBLEM

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[0007] Therefore, this invention aims at offering a water-color-ink constituent with still higher preservation stability in the water-color-ink constituent which contains without a dispersant in water the surface treatment pigment in which distribution and/or the dissolution are possible, improving printing stability.

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MEANS

[Means for Solving the Problem] The water-color-ink constituent of this invention is characterized by the multiple-valued anion concentration from which it is the water-color-ink constituent which contains without an aqueous medium and a dispersant in water at least the surface treatment pigment in which distribution and/or the dissolution are possible, and was isolated in said ink being 250 ppm or less.

[0009]

[Embodiment of the Invention] The water-color-ink constituent of invention distributes in water the surface treatment pigment in which distribution and/or the dissolution are possible without dispersants, such as a surfactant and water soluble resin, in an aqueous medium. Furthermore, the multiple-valued anion concentration which separated in ink adjusts to 250 ppm or less.

[0010] In this invention, even if a pigment does not use a dispersant, the condition of existing in stability with the minimum particle diameter which can be distributed underwater is expressed as "distribution and/or the dissolution." The minimum particle diameter which can be distributed is the minimum particle diameter which does not become small any more even if it increases distributed time amount. It is thought with the minimum particle diameter which can distribute a pigment that it distributes spontaneously so that water soluble dye may dissolve in water by the single molecule, because introduce a hydrophilic functional group in large quantities and it carries out surface treatment to the front face of carbon black or an organic pigment.

[0011] Surface treatment for "distributing and/or dissolving" is performed by combining hydrophilic functional groups, such as a carboxyl group, a carbonyl group, and hydroxyl, and the salt of those through direct or alkyl, alkyl ether, an aryl group, etc. on the surface of a pigment. The approach to which a pigment front face is made to specifically carry out the graft of the active species containing the approaches of oxidizing with an oxidizing agent and introducing [hydroxyl / a carboxyl group, / a carbonyl group, hydroxyl] a pigment front face underwater, these functional groups, or a functional group by chemical preparation is raised.

[0012] As for the water color ink of this invention, it is desirable to add a surface treatment pigment in 1 - 15% of range to the ink whole quantity. If it is this range, the water color ink of sufficient printing concentration can be obtained.

[0013] In the addition of an above-mentioned surface treatment pigment, if the isolation multiple-valued anion concentration in the ink of the water color ink of this invention is 250 ppm or less, even if it leaves ink for a long period of time, it does not have thickening etc., and can obtain ink with sufficient preservation stability. As a multiple-valued anion, sulfate ion, phosphoric-acid ion, and low-molecular polycarboxylic acid are mentioned. Since the sulfur contained in the pigment itself from the first ****s at a distributed process, it oxidizes by the halogen acid salt further used for the wet oxidation for surface treatment and serves as a sulfuric acid, it is easy to mix especially sulfate ion in large quantities. For this reason, removing to 250 ppm or less is desirable.

[0014] Reduction of the isolation multiple-valued anion concentration in ink has the desirable approach of creating ink, after refining the dispersion liquid of the surface treatment pigment oxidized and distributed by the reverse osmotic membrane, ultrafiltration, electrodialysis, etc. in order not to worsen the dispersibility of dispersion liquid. Moreover, it is also possible to refine,

after adding alkali, such as a sodium hydroxide, and creating a salt.

[0015] The quantum of isolation multiple-valued anion concentration can be performed by the following analytical method. An ultrafiltration filter separates ink into solid content and a liquid component, and a liquid component is diluted with ultrapure water to suitable concentration, and it measures by the ion chromatograph and is obtained.

[0016] In addition, if it does not **** even if it exists in the interior of a pigment, or adsorbs on a pigment front face strongly and leaves it, even if the whole quantity contained in the ink of the above-mentioned matter exceeds 250 ppm, the long-term preservation stability of ink will not be influenced.

[0017] As for this invention, it is desirable to use carbon black and an organic pigment as a pigment for carrying out surface treatment.

[0018] As an example of desirable carbon black, #20B, #40, MA100, etc. are mentioned as carbon black by Mitsubishi Chemical, Inc. by this invention. As Degussa AG carbon black, the color black FW18, the color black S170, the special black 250, etc. are mentioned. The KONDAKU tex SC, Rahaeng 1255, etc. are mentioned as carbon black by the Colombia carbon company. As carbon black by Cabot Corp., MONAKU 700, MONAKU 880, the elf tex 12, etc. are mentioned. In addition, these are the publications of an example of the suitable carbon black for this invention, and this invention is not limited by these.

[0019] As a desirable organic pigment, an azo system pigment, a phthalocyanine system pigment, an anthraquinone system pigment, the Quinacridone system pigment, a thioindigo system pigment, a triphenylmethane color system lake pigment, an oxazine system lake pigment, etc. are mentioned by this invention. Furthermore, if insoluble to an aqueous medium, the oil color, a disperse dye, etc. can also be used. Specifically as a yellow system, the C.I. pigment yellow 1, 2, 3, 4, 5, 6, 7, 10, 11, 12, 13, 14, 15, 16, 17, 65, and 83 is mentioned. moreover, as a red system C. I. pigment red 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 21, 22, 23, 30, 31, 32, 37, 38, 39, 40, 49, 50, 51, 52, 53, 55, 60, 64, 83, and 87, 88, 89, and 90, 112, 114, 123, 163 grades are mentioned. As a blue system, the C.I. pigment black 1 is mentioned as the C.I. pigment blues 2, 3, 15, 16, and 22, 25 grades, and a black system.

[0020] Moreover, creation of the surface treatment pigment used for the water color ink of this invention has especially the desirable thing that the approach to which a pigment front face is made to carry out the graft of the active species which contained the approaches of oxidizing with an oxidizing agent and introducing [hydroxyl / a carboxyl group / a carbonyl group hydroxyl] a pigment front face underwater, these functional groups, or a functional group by chemical preparation raises, and **** oxidizes and acquires for carbon black or an organic pigment with a halogen acid compound as mentioned above. As a halogen acid compound, a sodium-hypochlorite water solution, a calcium hypochlorite, a hypobromous acid sodium water solution, a hypoiodous acid sodium water solution, etc. are mentioned. In addition, since the following ** fluorine acid is very unstable, it cannot be substantially used for creation of a surface treatment pigment.

[0021] The aqueous medium of the water-color-ink constituent of invention is a medium for holding a surface treatment pigment, and can give the property as ink, and can add a fixing agent, pH regulator, an antioxidant and an ultraviolet ray absorbent, antiseptics, an antifungal agent, etc. further if needed including water, a moisturizer, and an osmosis accelerator at least.

[0022] Desirable water can use pure water, such as ion exchange water, ultrafiltration water, Milli Q water, and distilled water, or ultrapure water for this invention. Moreover, since generating of mold or bacteria can be prevented when carrying out the mothball of the ink constituent if the water which sterilized by UV irradiation or hydrogen-peroxide addition is used, it is suitable.

[0023] As a moisturizer which can be used for this invention It is chosen out of a water-soluble and hygroscopic high ingredient. A glycerol, ethylene glycol, A diethylene glycol, triethylene glycol, tetraethylene glycol, A polyethylene glycol, propylene glycol, dipropylene glycol, A polypropylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol 1,6-hexanediol, 1 and 2, 6-hexane triol, Polyols, such as pentaerythritol, 2-pyrrolidone, a N-methyl-2-pyrrolidone, Saccharides, such as ureas, such as RAKURAMU [, such as epsilon caprolactam,], urea, thiourea, ethylene urea, 1, and 3-dimethyl imidazolidinone, maltitol, a sorbitol, glucono lactone,

and a maltose, can be used.

[0024] These moisturizers can be added with the addition from which ink viscosity is set to 25 or less cPses at 25 degrees C together with other ink additives.

[0025] As an osmosis accelerator which can be used for this invention, permeability is brought forward by improving the wettability to a record medium, and it is chosen out of the water-soluble organic solvent and surfactant with which the surface tension of a water solution becomes small.

[0026] As a water-soluble organic solvent, 1, such as carbitol [, such as cellosolves, such as lower alcohol, such as ethanol and propanol, ethylene glycol monomethyl ether, and ethylene glycol monoethyl ether the diethylene-glycol monomethyl ether, diethylene glycol monoethyl ether, ethylene glycol mono—n-butyl ether, diethylene-glycol—n-butyl ether, and triethylene glycol—n-butyl ether,], 1, 2-hexandiol, 1, and 2-octanediol, and 2-alkyl diols are raised.

[0027] Moreover, as a surfactant, acetylene glycol system Nonion nature surfactants, such as the Nonion nature surfactants, such as anionic surfactants, such as fatty-acid salts and alkyl-sulfuric-acid ester salts, polyoxyethylene alkyl ether, and polyoxyethylene phenyl ether, and SAFI Norians 61 and 82,104,440,465,485 (all are trade name and air products – and made in – Chemicals above), a cationic surfactant, both ionic surfactants, etc. can be used.

[0028] In addition, without using for the surface treatment pigment of this invention the dispersant which consists of a surfactant, since it is the coloring agent in which distribution and/or the dissolution are possible, these surfactants used in the ink of this invention can be used for water only for promotion of osmosis. That is, although it is necessary to choose in the combination to which a pigment and each ingredient stick each other in order to usually give dispersibility to a pigment, by this invention, it can choose only by osmosis promotion nature, without taking combination into consideration.

[0029] Water-soluble resin can be used as a fixing agent. Water-soluble rosin Alginic acids, polyvinyl alcohol, hydroxypropylcellulose, A carboxymethyl cellulose, hydroxyethyl cellulose, methyl cellulose, Styrene-acrylic acid resin, styrene-acrylic-acid-acrylic ester resin, Styrene-maleic resin, styrene-maleic-acid half ester resin, Acrylic-acid-acrylic ester resin, isobutylene-maleic resin, rosin denaturation maleic resin, a polyvinyl pyrrolidone, gum arabic starch, the poly allylamine, a polyvinyl amine, polyethyleneimine, etc. are mentioned. In addition, without using for the surface treatment carbon black of this invention the dispersant which consists of water soluble resin, since it is the coloring agent in which distribution and/or the dissolution are possible, the water soluble resin used in the ink of this invention can be used for water only for fixing. That is, although it is necessary to choose in the combination to which a pigment and each ingredient stick each other in order to usually give dispersibility to a pigment, by this invention, it can choose only by fixable, without taking combination into consideration.

[0030] As a pH regulator, the hydroxide or amines of alkali metal, such as a lithium hydroxide, a sodium hydroxide, a potassium hydroxide, aqueous ammonia, triethanolamine, and diethanolamine, are mentioned.

[0031] as an anti-oxidant and an ultraviolet ray absorbent — aloha — NETO and methyl aloha – NETO etc. — aloha, the oxide of lanthanides, such as Ciba-Geigy Tinuvin(s) 328, 900, 1130, 384, 292, 123, 144, 622, 770, and 292, such as L-ascorbic acid, such as biurets, such as NETO, biuret, dimethyl biuret, and tetramethyl biuret, and a salt of those, Irgacor 252 and 153, Irganox 1010, 1076, and 1035, and MD1024, etc. is used.

[0032] As antiseptics and an antifungal agent, it can choose, for example from sodium benzoate, pentachlorophenol sodium, 2-pyridine thiol-1-oxide sodium, sodium sorbate, sodium-dehydroacetate, 1, and 2-JIBENJISO thiazoline-3-ON (pro cheating-on-the-fare XL- the pro cheating on the fare CRL of ICI, the pro cheating on the fare BDN, the pro cheating on the fare GXL, 2, pro cheating on the fare TN) etc.

[Translation done.]

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

EXAMPLE

[Example] (Example 1) MA8 (trade name, Mitsubishi Chemical, Inc. make) 100g was mixed in 1kg of water as carbon black, and the ball mill by zirconia beads ground. 400g of sodium-hypochlorite water solutions was added to this grinding undiluted solution, it boiled for 10 hours, and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. This wet cake was re-distributed in 5kg of water, and the ultrafiltration membrane of a cut off molecular weight 100,000 was used with the mini tongue (a trade name, Millipore Corp. make) of an ultrafiltration system, and it desalted and refined to electric conductivity 4 mS/cm, condensed to pigment concentration 15wt% further, and pigment dispersion liquid were adjusted.

[0034] The obtained pigment dispersion liquid were mixed as 30g and a moisturizing component, tert-pentanol 4g and Nissan Nonion NS-220(trade name, Nippon Oil & Fats Co., Ltd. make) 1g of the Nonion nature surfactant were mixed as glycerol 10g, 2-pyrrolidone 5g, and an osmosis promotion component, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.5. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and water color ink was prepared.

[0035] It is a centrifugal type ultrafiltration unit about water color ink. As a result of separating a liquid component using the ultra free-lancer 15/a cut off molecular weight 10,000 (a trade name, Nihon Millipore make) and measuring a liquid component by ion chromatograph DX-500 (Nippon Daionekusu make), the concentration of isolation multicharged ion was 105 ppm in sulfate ion.

[0036] It is a centrifugal type ultrafiltration unit about water color ink. As a result of separating a liquid component using the ultra free-lancer 15/a cut off molecular weight 10,000 (a trade name, Nihon Millipore make) and measuring a liquid component by ion chromatograph DX-500 (Nippon Daionekusu make), the concentration of isolation multicharged ion was 105 ppm in sulfate ion.

[0037] (Example 2) Demineralization / purification degree was performed by electric conductivity 10 mS/cm to the example 1, and water color ink was created similarly. The concentration of the sulfate ion which separated was 250 ppm.

[0038] (Example 3) Color black S170 (trade name, Degussa AG make) 40g was mixed in 1kg of water as carbon black, and the ball mill by zirconia beads ground. 400g of sodium-hypochlorite water solutions was added to this grinding undiluted solution, it boiled for 10 hours, and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. This wet cake was re-distributed in 5kg of water, and the ultrafiltration membrane of a cut off molecular weight 100,000 was used with the mini tongue (a trade name, Millipore Corp. make) of an ultrafiltration system, and it desalted and refined to electric conductivity 4 mS/cm, condensed to pigment concentration 15wt% further, and pigment dispersion liquid were adjusted.

[0039] The obtained pigment dispersion liquid were mixed as 35g and a moisturizer, diethylene-glycol-Monod n-butyl ether 7.5g was mixed as glycerol 10g, diethylene-glycol 5g, and an osmosis accelerator, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine

was added until Ink pH was further set to 7.3. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and water color ink was prepared.

[0040] As a result of analyzing water color ink by the same approach as an example 1, the concentration of the multiple-valued anion which separated was 200 ppm only in sulfate ion.

[0041] (Example 4) 50g of the C.I. pigment red 163 was mixed in 1kg of water as an organic pigment, and the ball mill by zirconia beads ground. 150g of sodium-hypochlorite water solutions was added to this grinding undiluted solution, and wet oxidation was performed, stirring for 10 hours. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. This wet cake was re-distributed in 5kg of water, and the ultrafiltration membrane of a cut off molecular weight 100,000 was used with the mini tongue (a trade name, Millipore Corp. make) of an ultrafiltration system, and it desalted and refined to electric conductivity 6 mS/cm, condensed to pigment concentration 15wt% further, and pigment dispersion liquid were adjusted.

[0042] SAFI Norian 465 of diethylene-glycol-Monod n-butyl ether 5g and an acetylene glycol system surfactant was mixed as 30g and a moisturizer, 1g was mixed for the obtained pigment dispersion liquid as glycerol 10g, diethylene-glycol 5g, and an osmosis accelerator, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.2. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and water color ink was prepared.

[0043] As a result of analyzing water color ink by the same approach as an example 1, the concentration of the multiple-valued anion which separated was 250 ppm only in sulfate ion. A part of C.I. pigment red 163 decomposes by oxidation of a hypochlorous acid, and sulfate ion is presumed to be desorption and the ionized thing.

[0044] (Example 1 of a comparison) Demineralization / purification degree was performed by electric conductivity 15 mS/cm to the example 1, and water color ink was created similarly. The sulfate ion concentration which separated was 300 ppm.

[0045] (Example 2 of a comparison) Demineralization / purification degree was performed by electric conductivity 20 mS/cm to the example 3, and water color ink was created similarly. The sulfate ion concentration which separated was 400 ppm.

[0046] MJ-930C (a trade name, Seiko Epson, Inc. make) of the <evaluation approach> (printing stability) piezoelectric-device type on-demand mold ink jet recording device was filled up with the ink of examples 1-4 and the examples 1 and 2 of a comparison, 3000 sheets of forms of A4 were printed continuously, and the stability at the time of printing was evaluated. the count of the need of the cleaning from the case where there is no turbulence of printing over all number of sheets — averaging — every 500 or more sheets — the case of being required — A — averaging — every [from 100 sheets] 500 sheets — the case where cleaning is required — B — less than 100 sheets estimated by setting to C the case where cleaning is required on the average.

[0047] (Preservation stability) The ink of examples 1-4 and the examples 1 and 2 of a comparison was left for one month at 60 degrees C, and the ink viscosity before and behind neglect was measured. The case where the viscosity change before and behind neglect was 95 - 105% of range was evaluated [% / 120 / B, less than 80%, or / or more] by being referred to as C in A and 80 - 120% of case.

[0048] The result of printing stability and preservation stability is collectively shown in Table 1.

[0049]

[Table 1]

実施例	遊離多価 アニオン濃度	印字安定性	保存安定性
実施例 1	1 0 5 p p m	A	A
実施例 2	2 5 0 p p m	A	B
実施例 3	2 0 0 p p m	A	A
実施例 4	2 5 0 p p m	A	B
比較例 1	3 0 0 p p m	A	C
比較例 2	4 0 0 p p m	B	C

[0050] In the examples 1-4 250 ppm or less, printing stability was A, and preservation stability is A or B and the multiple-valued anion concentration which was shown in Table 1 and from which it was isolated in the ink of the requirements for this invention like has offered the water-color-ink constituent with which printing stability and preservation stability were compatible. On the other hand, in the examples 1 and 2 of a comparison in which isolation multiple-valued anion concentration is over 250 ppm, as compared with the example, preservation stability was bad, and it has been incompatible in printing stability and preservation stability.

[Translation done.]